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(54) **Ammonia reduction-denitration process**

(57) The process comprises treating exhaust gases containing NO_x, consisting mainly of NO₂, with ammonia using a catalyst which is active to both a reaction of (NO₂ + NH₃ → N₂ + N₂O + H₂O) and a reaction of (N₂O + NH₃ → N₂ + H₂O) at an area velocity of 5 m/h or less and in a concentration ratio of NH₃/NO₂ of 1.3 or more. According to this process, it is possible to reduce NO₂ contained in the exhaust gases with ammonia at one stage without by-producing N₂O. The catalysts disclosed are H and/or Fe exchanged forms of zeolite.

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FIG.1

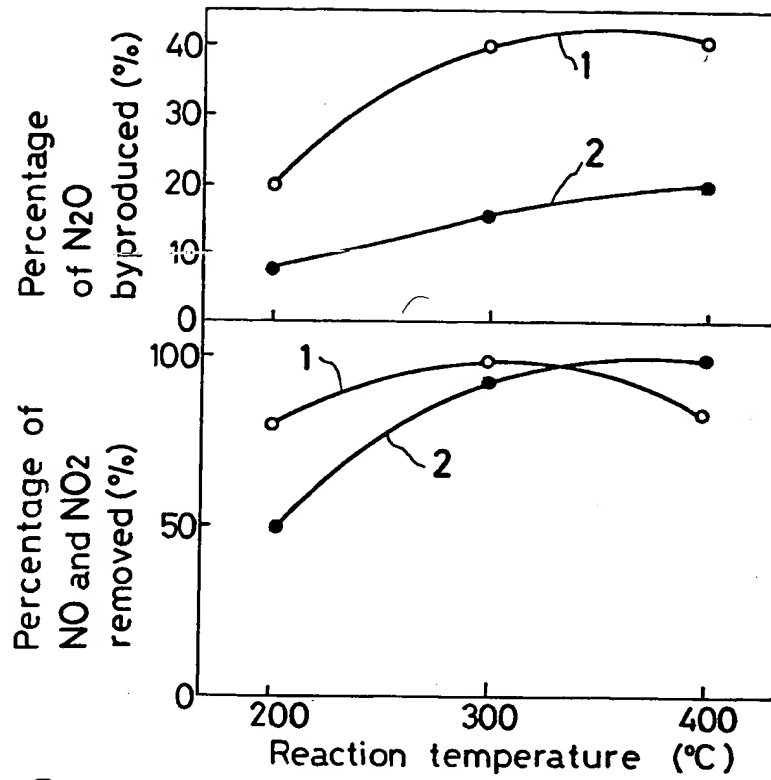
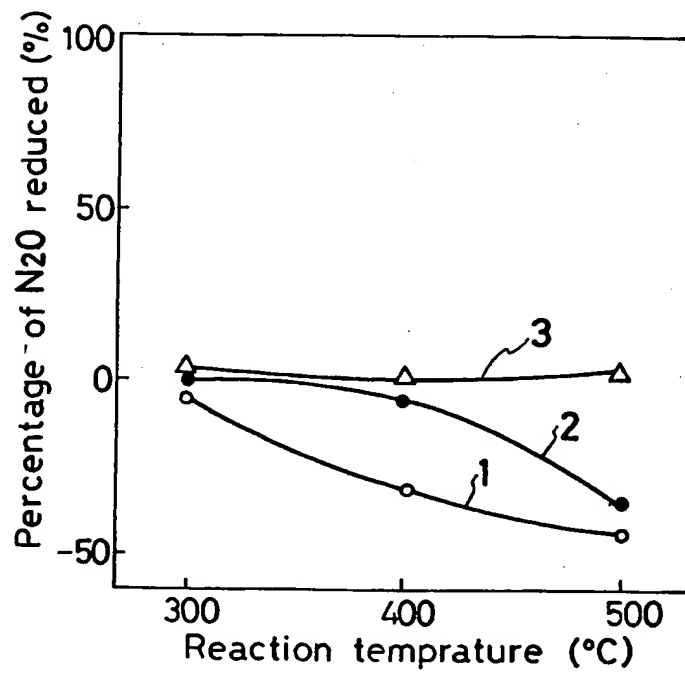


FIG.2



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FIG. 3

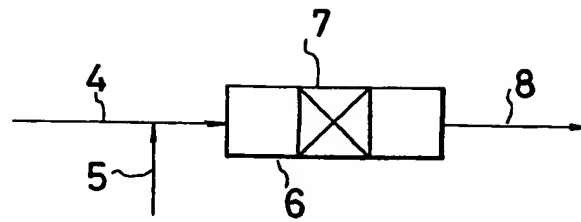


FIG. 4

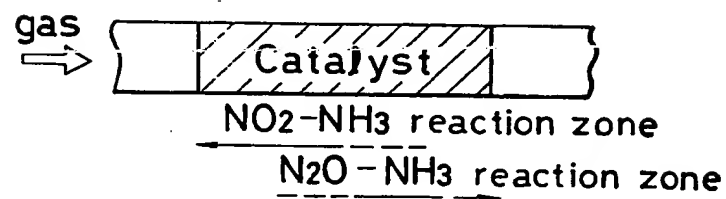


FIG. 5

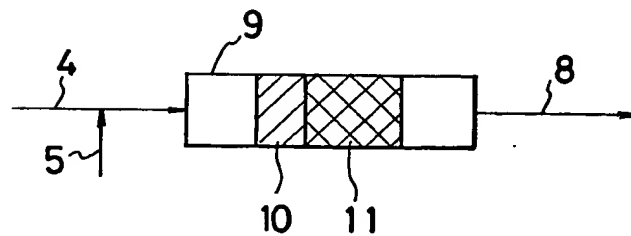


FIG. 6

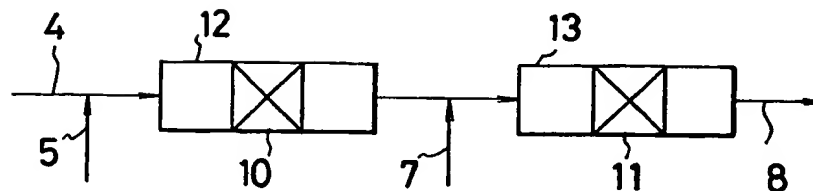


FIG. 7

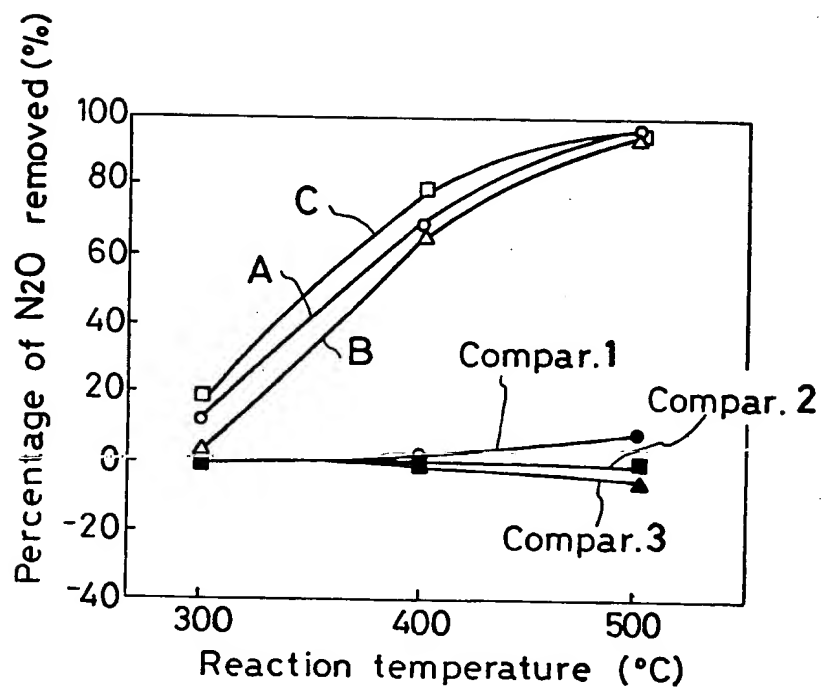


FIG. 8

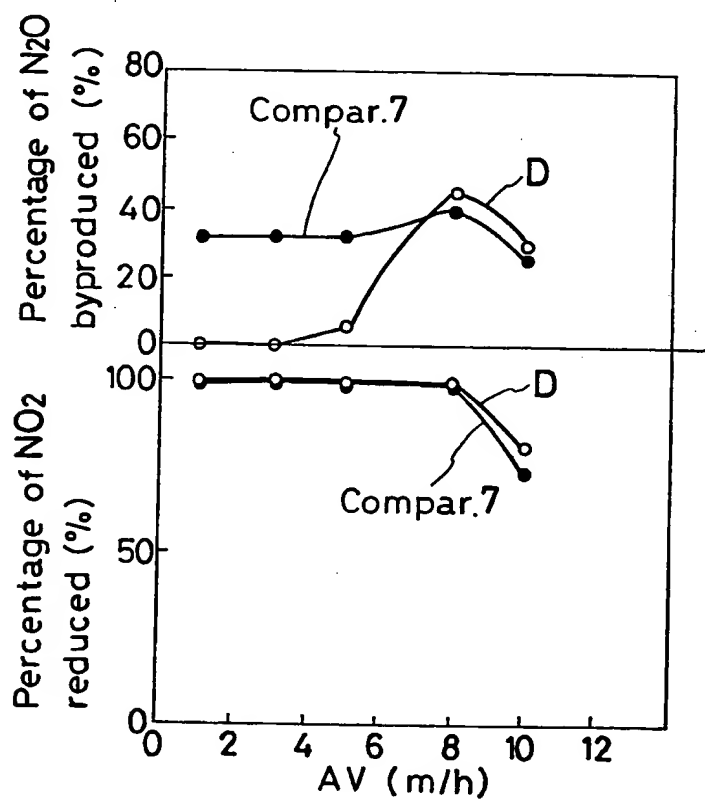


FIG.9

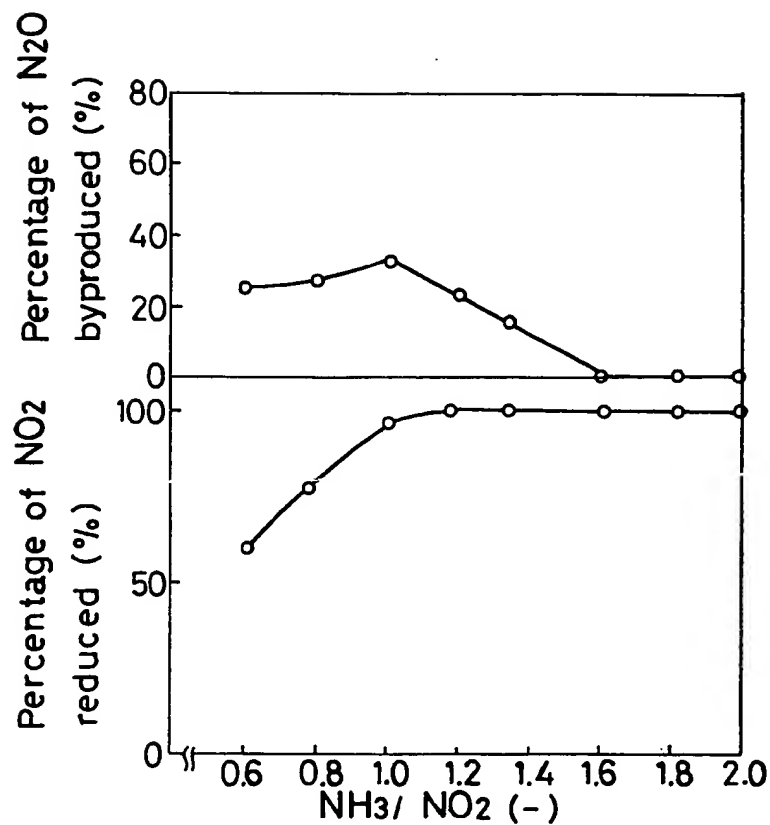
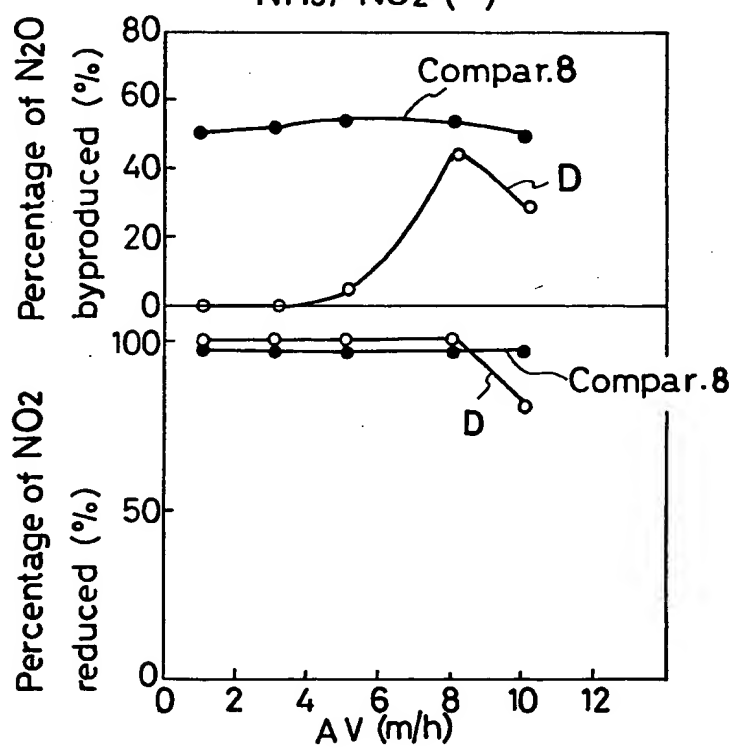


FIG.10



SPECIFICATION

Ammonia reduction-denitration process and apparatus therefor

5 This invention relates to a process for ammonia reduction-denitration of nitrogen oxides in exhaust gases and an apparatus therefor, and more particularly it relates to a denitration process suitable for controlling the concentration of nitrous oxide (dinitrogen oxide, N_2O), which is by-produced at the time of denitration, to a low level and also reducing nitrogen dioxide (NO_2) with ammonia, and an apparatus therefor.

The process of subjecting nitrogen oxides (NO_x) contained in exhaust gases to ammonia reduction with a catalyst into harmless nitrogen and water, i.e. the so-called catalytic ammonia reduction-denitration process, has a number of merits such as simple structure of apparatus, and has been practised for various purposes such as the denitration of exhaust gases from combustion apparatus e.g. large scale boilers. Further, as the catalyst used for the above process, those composed mainly of oxides of titanium (Ti), vanadium (V), tungsten (W), molybdenum (Mo), etc. and having superior performance and life together have been used in practice.

According to the studies of the present inventors, it has been found that the denitration process using the above catalysts is effective in the case where the nitrogen oxides consist of nitrogen monoxide (NO) or in the case where they consist of 50% or more of NO and 50% or less of nitrogen dioxide (NO_2). However, the process is not so effective in the case where they consist mainly of NO_2 or in the case where they contain nitrous oxide (N_2O). This will be explained referring to the accompanying drawings.

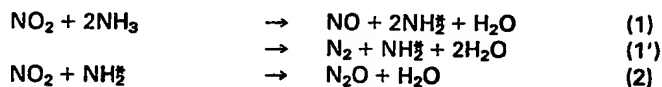
Figure 1 shows the results obtained when an exhaust gas having a proportion of NO_2 in NO_x of 80% (gas composition: NO_2 800 ppm, NO 200 ppm, NH_3 1,500 ppm, O_2 20%, H_2O 2%) was subjected to NH_3 reduction in the presence of conventional catalysts. In this Figure, numeral 1 represents the case of a $TiO_2-Co_2O_3$ catalyst and 2 represents the case of a $TiO_2-V_2O_5$ catalyst. As apparent from this Figure, while it is true that NO_2 and NO in the exhaust gas can be reduced, on the other hand, N_2O is by-produced in a large amount, so that the overall denitration performance is low. Thus, when the NH_3 reduction-denitration process is applied to nitrogen oxides consisting mainly of NO_2 , removal of the by-produced N_2O raises a serious problem.

Further, Figure 2 shows results obtained when N_2O (gas composition: N_2O 1,000 ppm, NH_3 1,000 ppm, O_2 20%, H_2O 2%) was subjected to NH_3 reduction in the presence of conventional denitration catalysts (numerals 1 and 2 in this Figure represent the same catalysts as the above and 3 represents a TiO_2-WO_3 catalyst). As apparent from this Figure, conventional denitration catalysts are not only inert to NH_3 reduction of N_2O , but also contrarily have a tendency of by-producing N_2O . Thus, when N_2O is included with NO or NO_2 as NO_x in the exhaust gas, N_2O remains as it is; hence in this case, too, removal of N_2O raises a serious problem.

The above-mentioned properties of conventional denitration catalysts have not been known previously, and the reason is considered to be as follows: the analytical method of determining the presence and amount of N_2O is so difficult that N_2O by-produced in the denitration reaction has not been studied and the evaluation of the denitration performance has been directed mainly to NO. Thus, no example of NH_3 reduction of N_2O has so far been attempted, and naturally any catalyst which is highly active to that reaction has never been found.

Exhaust gases from a nitric acid plant, metal-acid washing factory, nitrate-thermal decomposition furnace, etc. contain a high concentration of nitrogen oxides NO_x consisting mainly of NO_2 , and various processes for removing NO_x have been studied from the viewpoint of measures to counter public pollution or for the prevention of its effect on succeeding apparatus in the plant. Among these processes, an alkali-washing process has to date been practiced most often but this process suffers from problems in that the percentage of NO_x removed is low and waste water treatment is required. Thus, the development of a simple dry treatment process has been desired, such as a catalytic ammonia reduction-denitration process, yielding good results in the denitration of boiler flue gas.

However, when the catalytic ammonia reduction-denitration process is applied to the above mentioned exhaust gases there is raised a problem that N_2O is by-produced in a large amount; hence such an application cannot be a practical process. This is due to the fact that the most of NO_x in the above exhaust gas is in the form of NO_2 and in this respect, it has different properties from those of a boiler flue gas consisting mainly of nitrogen monoxide (NO). Namely, according to the results of the study carried out by the present inventors, the reaction of NO_2 with NH_3 proceeds by way of elementary reactions expressed by the following equations (1), (1') and (2) and is collectively expressed by the following equation (3):

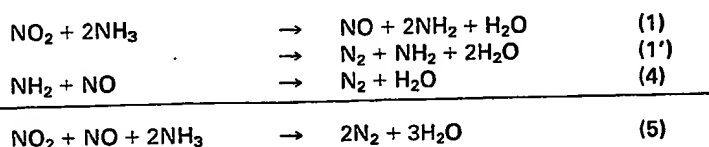


NH_2 : an intermediate adsorbed onto a catalyst

Since this reaction mechanism does not resort to any catalyst species, it is considered that even if any known denitration catalysts are used, the by-production of N_2O according to the equation (2) cannot be avoided so long as the process of NH_3 reduction-denitration of NO_2 is employed.

Further, it has been said that when highly reducing metals are washed with acids or dissolved in nitric acid, N_2O is generated in a large amount. As described above, a large number of plants need removal of N_2O including potential N_2O -generation sources from which N_2O is by-produced at the time of ammonia reduction-denitration; hence development of a process for selectively removing N_2O has been earnestly desired.

Thus, the present inventors made various studies on a process for reducing N_2O , and as a result proposed a process of converting a part of NO_2 into NO by a catalyst thermal decomposition in advance of its denitration reaction to thereby adjust the composition of NO_x in the exhaust gas to $(NO)/(total\ NO_x) \geq 0.5$, followed by subjecting the resulting gas to a conventional ammonia reduction-denitration reaction. This process is intended to have NH_3 consumed by NO as seen in the following equations to thereby inhibit the advance of the N_2O by-production reaction of the above equation (2):



This denitration process in a two-stage manner makes it possible to inhibit the N_2O by-production down to a level as low as several ppm and also is superior in principle, but the structure of apparatus as well as its control are complicated; hence a problem of its practical use is raised.

Thus, development of a denitration process capable of subjecting NO_2 to ammonia reduction at one stage as in the case of NO has been eagerly desired.

It is an object of the present invention to provide a highly active catalyst for the reduction reaction of N_2O by means of NH_3 and a process for ammonia reduction-denitration of N_2O by the use of the catalyst.

It is a further object of the present invention to provide a denitration process capable of subjecting NO_2 to NH_3 reduction at one stage without by-producing N_2O , and an apparatus therefor.

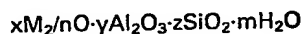
Accordingly, the present invention provides an ammonia reduction-denitration process for exhaust gases containing nitrogen oxides (NO_x), which process comprises treating said exhaust gases with ammonia by the use of a catalyst having an activity to both a formation reaction of nitrogen (N_2), nitrous oxide (N_2O) and water (H_2O) from nitrogen dioxide (NO_2) and ammonia (NH_3) and a formation reaction of N_2 and H_2O from N_2O and NH_3 , at an area velocity (the amount of gas/the total outer surface area of catalyst) of 5 m/h or less and in a ratio of NH_3 concentration to NO_2 concentration of 1.3 or more.

The present invention further provides an apparatus for ammonia reduction-denitration of exhaust gases containing nitrogen oxides (NO_x), which apparatus comprises a reaction vessel having filled therein a catalyst consisting of a compound having a zeolite structure expressed by the general formula



wherein x, y and z each represent an integer, M represents an optional metal element and n represents the valence of M, a part of the total of said M element being replaced by hydrogen or/and iron atoms.

The present invention further provides a catalyst for the ammonia reduction denitration exhaust gases containing nitrogen oxides (NO_x), the catalyst comprising a compound having a zeolite structure expressed by the general formula



wherein x, y and z each represent an integer, M represents an optional metal element and n represents the valence of M, a part or the total of said M element being replaced by hydrogen or/and iron atoms.

The present inventors have made studies on the activities of catalysts consisting of various metal oxides, upon the reaction of N_2O-NH_3 (see the following equation (6)):



As a result, it has been found that known catalysts comprising as their active component, oxides of transition metals such as vanadium (V), tungsten (W), chromium (Cr), manganese (Mn), cobalt (C), etc. cannot promote the ammonia reduction reaction of N_2O , whereas compounds obtained by replacing a part of the total of the alkali metals or alkaline earth metals contained in zeolites such as mordenite, Y type zeolite, etc. by iron (Fe) or hydrogen have a high activity for the ammonia reduction of N_2O .

Briefly the present invention is directed to an ammonia reduction-denitration process using a catalyst obtained by replacing the alkali metal or alkaline earth metal or natural or synthetic zeolites by hydrogen

or/and iron to impart an activity for the ammonia reduction of N_2O to the resulting material.

Further, the present invention is directed to an ammonia reduction-denitration process capable of denitrating NO_2 at one stage utilizing the fact that the above catalyst for ammonia reduction-denitration of N_2O is also active to the reaction of NO_2 with NH_3 (see the above equation (3)). Namely, the present invention is directed to a process wherein using the above catalyst and selecting the reaction conditions so as to give specific values, the reduction reaction of NO_2 by means of ammonia and also the ammonia reduction reaction of N_2O formed by the above reaction are successively advanced within the same catalyst layer to thereby make it possible to reduce NO_2 with ammonia at one stage without by-producing N_2O .

Embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings, in which:-

Figure 1 shows a chart illustrating the performances of conventional catalysts for the reduction of NO_2 with ammonia and the percentage of N_2O by-produced;

Figure 2 shows a chart illustrating the performances of conventional catalysts for the reduction of N_2O with ammonia;

Figure 3 shows a schematic view illustrating the denitration apparatus employed in the present invention;

Figure 4 shows a view illustrating the present invention in principle;

Figures 5 and 6 each show a view illustrating a reactor as an embodiment of the present invention;

Figure 7 shows a chart illustrating the performances of the catalyst of the present invention and a comparison catalyst for the reduction of N_2O with ammonia;

Figure 8 shows a chart illustrating comparison results of Example 1 of the present invention and Comparative example 7;

Figure 9 shows a chart illustrating results of Example 11 of the present invention; and

Figure 10 shows a chart illustrating results of Example 10 of the present invention.

It is important for the catalyst used in the present invention that Fe or/and H ions are incorporated into the skeleton structure of zeolite. Namely, the substitution ions contained in the hydrogen and/or iron substitution type zeolite catalyst according to the present invention have specific properties and exhibit chemically entirely different behaviour from that of ions contained in metal oxides alone or metal oxides supported on a carrier; hence the catalyst is also essentially different from iron oxide catalysts supported on alumina, silica or silica alumina.

In general, zeolites are aluminosilicates having a complicated skeleton structure, as described in "Zeolites, their base and applications" edited by Hara et al and published from Kohdansha (1980), and expressed by the general formula $xM_2/nO \cdot yAl_2O_3 \cdot zSiO_2 \cdot mH_2O$ wherein M represents an optional metal element such as Na, K, Ca, etc. and n represents their valence. This metal element M is usually an alkali metal or an alkaline earth metal and these can be replaced by hydrogen, other transition metal cations or the like. The zeolites usable in the present invention may be any of those having the above properties, but those having a ratio of SiO_2/Al_2O_3 of 3 or more i.e. the so-called high silica zeolites are preferably from the viewpoint of the heat resistance and activity of catalyst, and preferred examples are mordenite, clinoptilolite, faujasite, zeolite Y, etc. Further, as to the method of hydrogen or iron substitution in the above zeolites, immersing in an acid solution and/or an iron salt solution, for example, is employed and also any methods which can attain the object may be employed in the present invention, so long as hydrogen or/and iron substitution type zeolites retaining the skeleton structure of zeolites are obtained thereby.

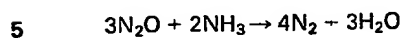
Typically, the catalyst of the present invention may be prepared by immersing a natural or synthesized zeolite such as mordenite, clinoptilolite, faujasite, etc. in hydrochloric acid, ammonium chloride (NH_4Cl) in aqueous solution, ferric chloride ($FeCl_3$) in aqueous solution or ferric nitrate $Fe(NO_3)_3$ in aqueous solution, to replace the alkali metal or alkaline earth metal ion contained in the above zeolite by a hydrogen or/and an iron ion, followed by calcination at about $500^\circ C$. In this case, when a mixed aqueous solution of ammonium chloride and ferric chloride is used, a catalyst wherein the alkali metal or alkaline earth metal is replaced by hydrogen more than iron is obtained; when ferric nitrate aqueous solution is used, a catalyst is obtained wherein the metal is replaced almost entirely by iron rather than by hydrogen; and when a combination of ammonium chloride aqueous solution with ferric nitrate aqueous solution is used, a catalyst wherein the metal is replaced by iron more than hydrogen is obtained.

Next, a flow sheet in the case where the catalyst according to the present invention is used for denitration of a N_2O -containing gas is shown in Figure 3. An exhaust gas led through piping 4 has ammonia injected through piping 5, enters a catalyst layer 7 inside a reactor 6 wherein N_2O contained in the gas is easily reduced by ammonia into harmless nitrogen and water, and is exhausted through piping 8.

Further, the principle in which NO_2 is denitrated into N_2 at one stage by the use of the above catalyst will be described below.

As shown in Figure 4, when ammonia reduction of NO_2 is carried out employing a reactor being filled with a large amount of a catalyst which is active to both the reaction of NO_2 with NH_3 of the above equation (3) and the ammonia reduction reaction of N_2O , and under a condition where ammonia is injected in large excess of a necessary amount for the reaction of the equation (3), then two reaction zones are formed inside the catalyst layer, as shown in the Figure. Namely in the vicinity of the inlet of the catalyst layer, the equation (3) having a higher reaction rate proceeds predominantly to form a first reaction zone wherein N_2 , N_2O and water are formed from NO_2 and NH_3 , i.e. a reaction zone of NO_2-NH_3 . Since the catalyst layer is elongated enough, NO_2 formed therein and NH_3 injected in excess and remaining without being consumed in the

reaction of the equation (3) are reacted into N_2 and H_2O by the function of the catalyst which is also provided with the activity to catalyse the NH_3 reduction of N_2O , as shown in the equation (6), to form a second reaction zone i.e. a zone of ammonia reduction of N_2O .



(6)

5

As described above, when a catalyst species and the reaction conditions are suitably selected, it is possible to reduce NO_2 with ammonia into N_2 and H_2O using a single catalyst layer.

In the denitration process of the present invention, the catalyst and the reaction conditions are selected as follows:

10 First, the catalyst used should be active to both the reaction of NO_2-NH_3 of the equation (3) and the reduction reaction of N_2O of the equation (6). Examples of such a catalyst are H and/or Fe substitution type zeolite catalysts, and particularly, the above-mentioned high silica zeolite catalysts such as mordenite, zeolite Y, etc. are preferred.

15 Secondly, as for the amount of NH_3 injected, it is necessary to select an amount of NH_3 sufficient for completing the two reactions of the equations (3) and (5). Thus, it is preferred to select the ratio of the amount of NH_3 injected, to the total amount of NO_x contained in the gas (denoted as NH_3/NO_x) so as to give stoichiometrically 1.3 or more, particularly 1.6 or more.

20 Thirdly, it is necessary to have sufficient catalysts so that the above two reaction zones can be formed inside the catalyst layer. Thus, in the case of the above catalysts, it is preferred to select the area velocity AV (the amount of gas to be treated/the total outer surface area of catalyst) so as to give a value of 5 or less, particularly 3 or less.

When the above three conditions are satisfied, it is possible to reduce NO_2 with ammonia into N_2 and H_2O under inhibition of the amount of N_2O by-produced.

25 As for the reactor employed in the present invention, a reactor as shown in Figure 4 being filled with a single catalyst which is active to both the reaction of NO_2-NH_3 and that of N_2O-NH_3 may be employed. Further, a reactor as shown in Figure 5 may also be employed wherein a catalyst layer 10 having a superior activity to catalyse the reaction of NO_2-NH_3 of the equation (3) is provided on the upstream side of the reactor 9 and a catalyst layer 11 having a superior activity to catalyse the reaction of N_2O-NH_3 is provided on the downstream side thereof, whereby the total amount of catalyst used can be reduced. In this Figure, numeral 30 4 represents a piping for gas to be treated; 5, a piping for ammonia injection; and 8, a piping for treated gas.

Next, Figure 6 shows another flow sheet in the case where the catalyst of the present invention is used for denitration of a NO_2 -containing gas. A NO_2 -containing gas led through piping 4 has ammonia injected through ammonia-injecting piping 5, and is then led into a reactor 12 having a known denitration catalyst such as oxides of Ti, V, W and/or Mo filled therein, wherein it is reduced with ammonia into nitrogen and 35 N_2O and water according to the equation (3). The exhaust gas further has ammonia injected through ammonia-injecting piping 7 and then led into a reactor 13 having a catalyst 11 according to the present invention filled therein, wherein N_2O is reduced with ammonia as shown in the above equation (6). Thus, even a gas consisting mainly of NO_2 can be subjected to denitration treatment without by-producing N_2O .

40 The present invention will be described in more detail by way of Examples, which do not limit the scope of the present invention.

Examples 1 to 3 (examples of catalyst preparation)

45 The respective powders of mordenite, faujasite and zeolite Y, each in an amount of 10 g, were immersed in 100 ml of a mixed aqueous solution of ammonium chloride and ferric chloride (NH_4Cl 50g/l, $FeCl_3$ 10g/l) for 24 hours, followed by washing with 1ℓ of water, filtering and drying at 150°C. The resulting respective powders were shaped into tablets of 10 mm in diameter and 5 mm thick under a total pressure of 3 tons, followed by calcination at 500°C for 2 hours to obtain catalysts of the present invention A, B and C.

50 Examples 4 to 6 (Examples of catalyst preparation)

Example 1 was repeated except that the mixed solution of ammonium chloride-ferric chloride was replaced by ferric nitrate ($Fe(NO_3)_3$) aqueous solution (amount used: 20 g/l, 58g/l and 1g/l), and mordenite powder (10 g in each case) was immersed in these solutions, to obtain catalyst of the present invention D, E and F.

55 Examples 7 to 9 (Examples of catalyst preparation)

The respective powders of mordenite, faujasite and zeolite Y (each 10 g) were immersed in an ammonium chloride aqueous solution (50 g/l) for 24 hours, followed by washing with 1ℓ of water, filtering, further immersing the resulting respective slurries in a ferric nitrate aqueous solution (1 g/l) and carrying out the 60 same procedure as in Example 1, to obtain catalysts of the present invention G, H and I.

Comparative Examples 1 to 6 (Preparation of examples of comparison catalysts)

Mordenite, faujasite and zeolite Y used in Examples 1 to 9 were made comparison catalysts, respectively. Further, ferric nitrate (1g) and water (3 ml) were added to the respective powders of α - Al_2O_3 , silica alumina (SiO_2 70 wt. %, Al_2O_3 wt. %) and titanium oxide (TiO_2) (each 10g) and the respective mixtures were kneaded in a mortar, followed by drying, shaping and calcination as in Example 1 to obtain comparison catalysts 4, 5 and 6.

The catalysts obtained in the above Examples and Comparative examples were respectively milled into from 10 to 20 meshes, and using these milled materials, their activities to ammonia reduction reaction of N_2O were observed under the following conditions:

- (1) gas composition:
- | | |
|----------------------|-----------|
| N_2O | 1,000 ppm |
| NH_3 | 1,000 ppm |
| O_2 | 20% |
| H_2O | 2% |
| N_2 | remainder |
- (2) Space velocity (SV) : $10,000 \text{ h}^{-1}$
- (3) Reaction temperature: 300 to 500°C
- (4) N_2O analytical method: infrared spectrophotometry

Figure 7 shows the respective performances of ammonia reduction of N_2O , of catalysts A, B and C of Examples 1 to 3 and comparison catalysts. In this Figure, A, B and C represent catalysts of the present invention A, B and C, respectively and Comparison 1, Comparison 2 and Comparison 3 represent Comparison catalysts 1, 2 and 3, respectively. As seen from the results shown in this Figure, the comparison catalyst containing iron oxide as an active component and the zeolite catalysts not subjected to hydrogen and iron substitution (Comparative examples 1 to 3) have no activity to ammonia reduction of N_2O , whereas any of the hydrogen and iron substitution zeolite catalysts A, B and C have a high activity to reduction of N_2O .

Further, the following Table 1 shows the percentages of N_2O removed at 450°C of catalysts of Examples 1 to 9 and Comparison catalysts 1 to 6, and the substitution percentages of hydrogen or iron based on the results of elemental analysis. As seen from this Table, when the alkali metal or alkaline earth metal contained in the zeolites is replaced by hydrogen or iron, the activity to the ammonia reduction of N_2O is notably improved. Further, it is seen that when all of the exchangeable cations are not replaced by iron but replaced by both iron and hydrogen, a high activity is exhibited.

TABLE 1

5			Catalyst	Name of zeolite	Substitution percentage %		Percentage of N ₂ O removed at 450°C (%)	5
					H	Fe		
10	Example	1	A	mordenite	42	35	86	10
		2	B	faujasite	51	29	84	
		3	C	zeolite Y	55	40	94	
		4	D	mordenite	4	84	75	
		5	E	mordenite	2	51	63	
15		6	F	mordenite	2	37	21	15
		7	G	mordenite	25	61	97	
		8	H	faujasite	20	71	93	
		9	I	zeolite Y	12	81	99	
20	Compar. Example	1	Compar. catalyst 1	mordenite	1	5	5	20
		2	Compar. catalyst 2	faujasite	0.5	6	-2	
		3	compar. catalyst 3	zeolite Y	< 0.1	< 0.1	0	
25		4	compar catalyst 4	—	—	—	-45	25
		5	Compar. catalyst 5	—	—	—	-35	
30		6	Compar. catalyst 6	—	—	—	-33	30

* Substitution percentage: Equivalent % of H and Fe to total M in $xM_2/nO \cdot yAl_2O_3 \cdot zSiO_2 \cdot mH_2O$

35 According to Examples 1 to 9, N₂O which could have never been reduced with ammonia can be denitrated by ammonia reduction. Further, N₂O generated in the case where NO₂ is contained in a high proportion as in the case of exhaust gas from a nitric acid plant, can be removed by means of the catalyst of the present invention.

40 Next, Examples of ammonia reduction-denitration of NO₂-containing gas by the use of the catalyst of the present invention will be described below.

Example 10

45 Tablets of a H, Fe-mordenite catalyst obtained by replacing 42 equivalent % of Na, K and Ca contained in mordenite by hydrogen (H) and 35 equivalent % thereof by iron (Fe) were ground, followed by adjusting the particle size to from 10 to 20 meshes. The resulting particles (50 ml) were filled in a quartz glass reaction tube of 30 mm in inner diameter, and a test of ammonia reduction of NO₂ was carried out under the following conditions to observe the percentage of NO₂ reduced and the percentage of N₂O by-produced:

50 Test conditions:

(1) gas composition

55 NO₂ 1,000 ppm
NH₃ 1,800 ppm (NH₃/NO₂ = 1.8)
O₂ 20 %
H₂O 2 %
N₂ remainder

(2) Reaction temperature: 450°C

60 (3) Area velocity AV: 10, 7, 5, 3 and 1 m/h

For the analysis of NO₂ and N₂O, a NO_x meter employing chemiluminescence and infrared spectrophotometry was employed. The percentage of NO₂ reduced and the percentage of N₂O by-produced are defined by the following equations:

Percentage of NO₂ reduced (%)

$$= \frac{\left(\text{NO}_2 \text{ concentration at inlet of catalyst layer} \right) - \left(\text{NO}_x \text{ concentration at exit of catalyst layer} \right)}{\left(\text{NO}_2 \text{ concentration at inlet of catalyst layer} \right)} \times 100$$

Percentage of N₂O by-produced (%)

$$= \frac{\left(\text{N}_2\text{O concentration at exit of catalyst layer} \right)}{\left(\text{NO}_2 \text{ concentration at inlet of catalyst layer} \right)} \times 100$$

20 Comparative example 7

A test was carried out in the same manner as in Example 10 except that among the test conditions of Example 10, the NH₃ concentration was changed to 1,000 ppm (NH₃/NO₂ = 1.0).

Figure 8 shows test results of Example 10 and Comparative example 7. In this Figure, D represents the case of Example 10, and Comparison 7, that of Comparative example 7. As seen from this Figure, the process of the present invention (Example 10) is very effective for reducing the amount of N₂O by-produced at the time of ammonia reduction-denitration of NO₂. Further, it is seen that in the case of Example 10 where NH₃ concentration is high, as the AV is reduced (i.e. the contact time is increased), NO₂ reduction and increase in the amount of N₂O by-produced first occurs followed by N₂O reduction due to the NH₃ reduction of N₂O, whereas in the case of Comparative example 7 where the NH₃ concentration is low, the NH₃ reduction of N₂O cannot proceed, and to whatever extent the AV value is reduced, no N₂O reduction is effected.

Further, as seen from the results of this Figure, the AV value defining the present invention is preferably 5 or less, more preferably 3 or less.

Example 11

A test was carried out in the same manner as in Example 10 except that in the test conditions of Example 10, AV=1.0 m/h, and NH₃ concentration = 500 to 2,000 ppm.

Figure 9 shows the results of Example 11. As seen from this Figure, it is preferred in order to inhibit N₂O by-production that the ratio of NH₃/N₂O be 4/3 or more, particularly 1.6 or more, in terms of stoichiometrical value.

Comparative Example 8

A test was carried out in the same manner as in Example 10 except that a titanium oxide-vanadium pentoxide catalyst (TiO₂-V₂O₅ catalyst) generally used for the process of ammonia reduction-denitration of NO was used as catalyst.

Figure 10 shows results of Example 10 and Comparative example 8 for comparison. In this Figure, D represents the case of Example 10 and Comparison 8, that of Comparative example 8. As seen from this Figure, the process of the present invention wherein a catalyst having a high N₂O decomposition percentage is used under specified conditions is also effective.

50 Examples 12 to 14

Tests were carried out in the same manner as in Example 10 except that in the test conditions of Example 10, AV was made a constant value of 3 m/h and the respective hydrogen and iron substitutes of mordenite, faujasite and zeolite Y were used as catalyst. The hydrogen and iron substitution percentages of the respective catalysts expressed in terms of equivalent % to the total amount of Na, K or Ca contained in the

55 respective starting zeolites are shown in the following Table 2:

TABLE 2

5	Name of catalyst	Percentage substitution (%)		5
		H	Fe	
	H and Fe substitution type mordenite	25	64	
	H and Fe substitution type faujasite	35	45	
10	H and Fe substitution type zeolite Y	40	53	10

Table 3 collectively shows the performance of catalysts of Examples 12 to 14. As seen from the results, the hydrogen and ion substitution type zeolites yield good results in carrying out the present invention. 15

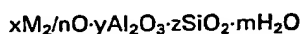
TABLE 3

20	No. of Example	Percentage of NO ₂ reduced (%)	Percentage of N ₂ O by-produced (%)	20
	12	99.7	0.1 or less	
	13	99.6	0.1 or less	
	14	99.9	0.1 or less	

As described above, according to the present invention, a catalytic ammonia reduction-denitration treatment of exhaust gases containing NO_x consisting mainly of NO₂ has become possible. 25

CLAIMS

- 30 1. An ammonia reduction-denitration process for exhaust gases containing nitrogen oxides (NO_x), which process comprises treating said exhaust gases with ammonia by the use of a catalyst having an activity to both a formation reaction of nitrogen (N₂), nitrous oxide (N₂O) and water (H₂O) from nitrogen dioxide (NO₂) and ammonia (NH₃) and a formation reaction of N₂ and H₂O from N₂O and NH₃, at an area velocity (the amount of gas/the total outer surface area of catalyst) of 5 m/h or less and in a ratio of NH₃ concentration of NO₂ concentration of 1.3 or more. 35
2. An ammonia reduction-denitration process according to Claim 1, wherein said catalyst is a hydrogen and/or iron substitution type zeolite.
3. An ammonia reduction-denitration process according to Claim 2, said zeolite is selected from the group consisting of mordenite, clinoptilolite, faujasite and zeolite Y. 40
4. An ammonia reduction-denitration process according to any of Claims 1 to 3, wherein the catalyst comprises a compound having a zeolite structure expressed by the general formula

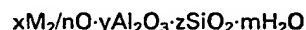


- 45 wherein x, y and z each represent an integer, M represents an optional metal element and n represents the valence of M, a part or the total of said M element being replaced by hydrogen or/and iron atoms.
5. An ammonia reduction-denitration process according to any one of Claims 1 to 4, wherein there is employed a reactor having a second catalyst which is active to the formation reaction of N₂, N₂O and H₂O from NO₂ and NH₃, filled therein upstream and also having the said catalyst which is active to both a formation reaction of N₂, N₂O and H₂O from N₂O and NH₃ and a formation reaction of N₂ and H₂O from N₂O and NH₃, filled therein downstream. 50
6. An ammonia reduction-denitration process according to Claim 5, wherein said second catalyst which is active to the formation reaction of N₂, N₂O and H₂O from NO₂ and NH₃ is at least one selected from the group consisting of oxides of Ti, V, W and Mo, and the first-mentioned catalyst which is active to both the formation reaction of N₂, N₂O and H₂O from N₂O and NH₃ and the formation reaction of N₂ and H₂O from N₂O and NH₃ is a hydrogen and/or iron substitution-type zeolite. 55
7. An apparatus for ammonia reduction-denitration of exhaust gases containing nitrogen oxides (NO_x), which apparatus comprises a reaction vessel having filled therein a catalyst consisting of a compound having a zeolite structure expressed by the general formula 60



- wherein x, y and z each represent an integer, M represents an optional metal element and n represents the valence of M, a part of the total of said M element being replaced by hydrogen or/and iron atoms. 65

8. A catalyst for the ammonia reduction denitration of exhaust gases containing nitrogen oxides (NO_x), the catalyst comprising a compound having a zeolite structure expressed by the general formula



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wherein x, y and z each represent an integer, M represents an optional metal element and n represents the valence of M, a part or the total of said M element being replaced by hydrogen or/and iron atoms.

5

9. An ammonia reduction-denitration process for exhaust gases containing nitrogen oxides (NO_x) substantially as hereinbefore described in any one of Examples 1 to 14 with reference to the accompanying drawings.

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10. An ammonia reduction-denitration process for exhaust gases containing nitrogen oxides (NO_x) as claimed in Claim 1 substantially as hereinbefore described with reference to the accompanying drawings.

11. An apparatus for ammonia reduction-denitration of exhaust gases entering nitrogen oxides (NO_x) as claimed in Claim 7 substantially as hereinbefore described with reference to any one of Figures 3 to 6.

12. An apparatus for ammonia reduction-denitration of exhaust gases containing nitrogen oxides (NO_x) substantially as hereinbefore described and with reference to any one of Examples 1 to 14.

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13. A catalyst for ammonia reduction-denitration of exhaust gases containing nitrogen oxides (NO_x) substantially as hereinbefore described in any one of Examples 1 to 14.

14. A catalyst for the ammonia reduction-denitration of exhaust gases containing nitrogen oxides (NO_x) as claimed in Claim 8 substantially as hereinbefore described.

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